Fundamental Studies of Lithium-Sulfur Cell Chemistry

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LBNL

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Project ID # ES224

Overview

Timeline

- Project start: Oct 1 2013
- Project end: Sept 30 2018
- Percent complete: 70%

Barriers

- Barriers addressed
  - Energy density
  - Cycle life

Budget

- Total project funding
  - DOE share ($ 2,000,000)
  - Contractor share ($ 0)
- Funding FY14: $500,000
- Funding FY15: $500,000

Partners

- ALS, SSRL, Molecular Foundry, NRSC
- Lead Institution: LBNL

Relevance and Objectives

Project Objective: To provide a fundamental science-based understanding of the products of redox reaction products (polysulfides) in a sulfur cathode, and enable rational design strategies to exploit the high energy density of lithium-sulfur cells.

FY15 Objectives: Build and cycle full cells for *in situ* XAS experiment to study the redox reactions at the front and the back of a Sulfur Cathode.

- Simulated X-ray Absorption Spectroscopy (XAS): Complete solubility calculations for polysulfide dianions and radical anions in different solvents. Complete Thermodynamic calculations of S encapsulated in carbon nanospheres
- In situ Cell for Measurement of XAS Spectra: Perform in situ measurements of XAS spectra of a Li-S cell.
- Mechanistic Insight: Compare simulations and experiments to obtain mechanistic insight into the redox chemistry of sulfur.
- Cathode and Cell Design: Build *in situ* cells to directly probe cathode from the back of the cathode.

Milestones

Month/Year	Milestone or Go/No-Go	Description	Status
Feb. 15, 2016	milestone	First principle calculation of the stability of lithium polysulfides	completed
May 20, 2016	milestone	Build and test *in situ* XAS cell to directly probe cathode side of Li-S cell.	completed
Sep. 23, 2016	milestone	Quantitative comparison of experimental and theoretical XAS spectra	completed

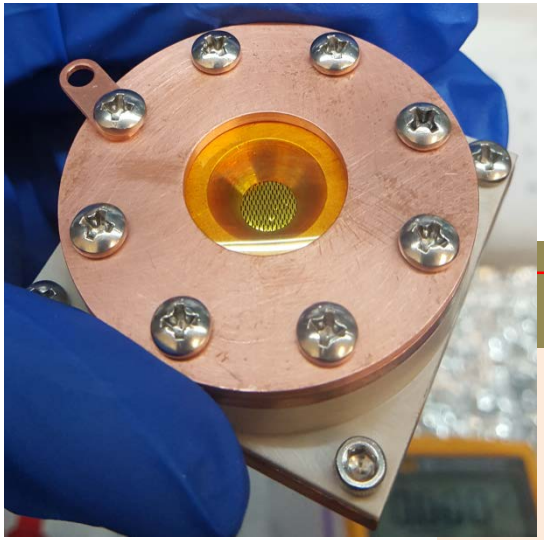
Milestones

Month/Year	Milestone or Go/No-Go	Description	Status
Dec, 15, 2016	milestone	Calculate the thermodynamic properties of a cathode with sulfur confined within carbon nanospheres	completed
June 20, 2017	milestone	Examine the effect of cycling rate and cathode thickness on the redox reactions in a Li-S battery	on track
Sep 23, 2017	milestone	First study of in situ Li-S reaction with polysulfides confined within cathode using a fluorinated polyether membrane	on track

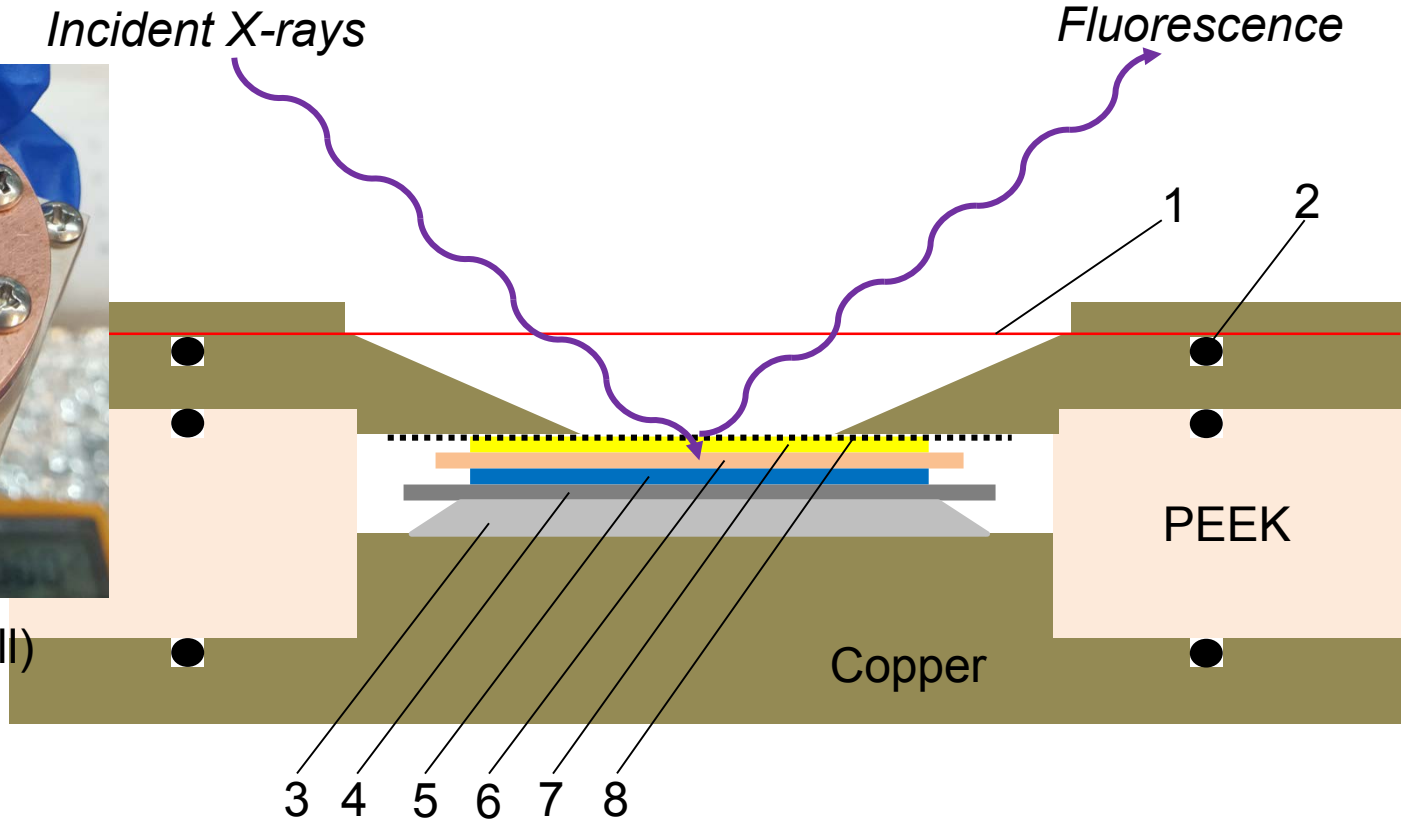
Approach

- First implementation of a first-principles framework for understanding products in sulfur cathodes.
- Calculation of X-ray spectra of polysulfides based on molecular dynamics simulations and excited electron and Core Hole (XCH) method.
- Conduct complementary X-ray spectroscopy experiments to obtain molecular insight into the nature of polysulfide speciation and their fingerprints.
- Design lithium-sulfur cells with SEO electrolytes for enabling *in situ* study of redox reactions at the sulfur cathode.
- Build *in situ* XAS cells that enable directly probing the back of the cathode to determine redox reactions happening at the back of a thick cathode.
- Modify the design of lithium-sulfur cells with perfluoro polyether electrolytes for enabling *in situ* study of redox reactions at the front of sulfur cathodes

Technical Accomplishment: Built in situ XAS cell to directly probe cathode side of Li-S cell

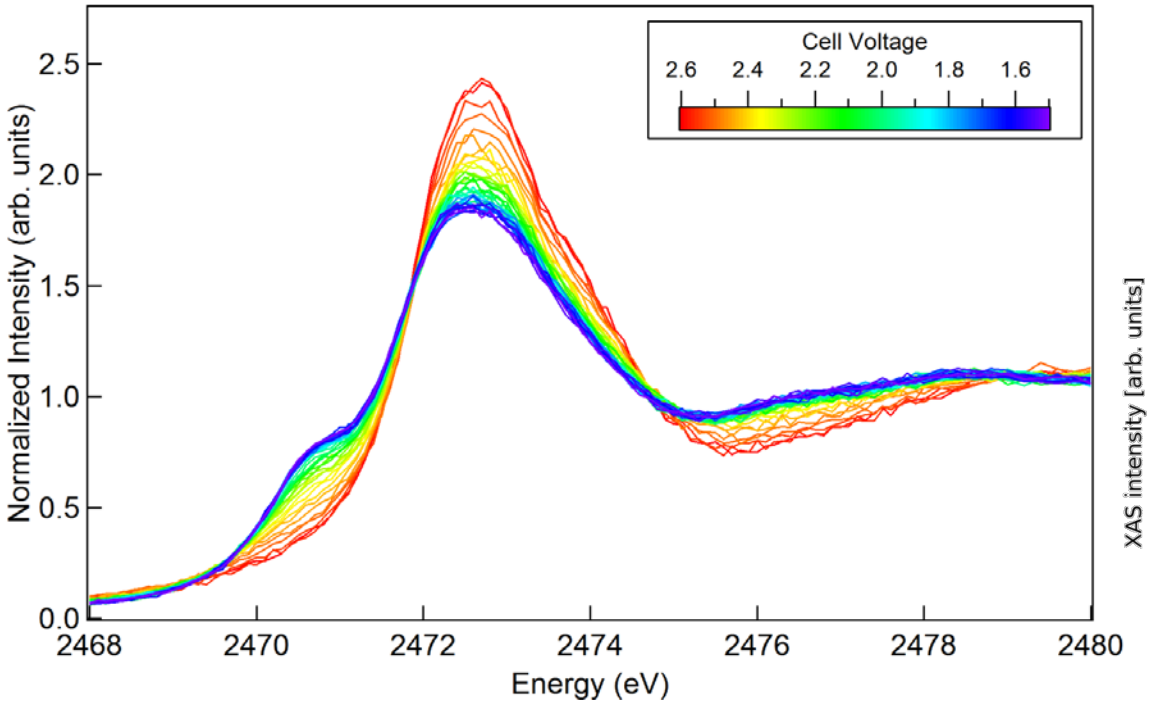


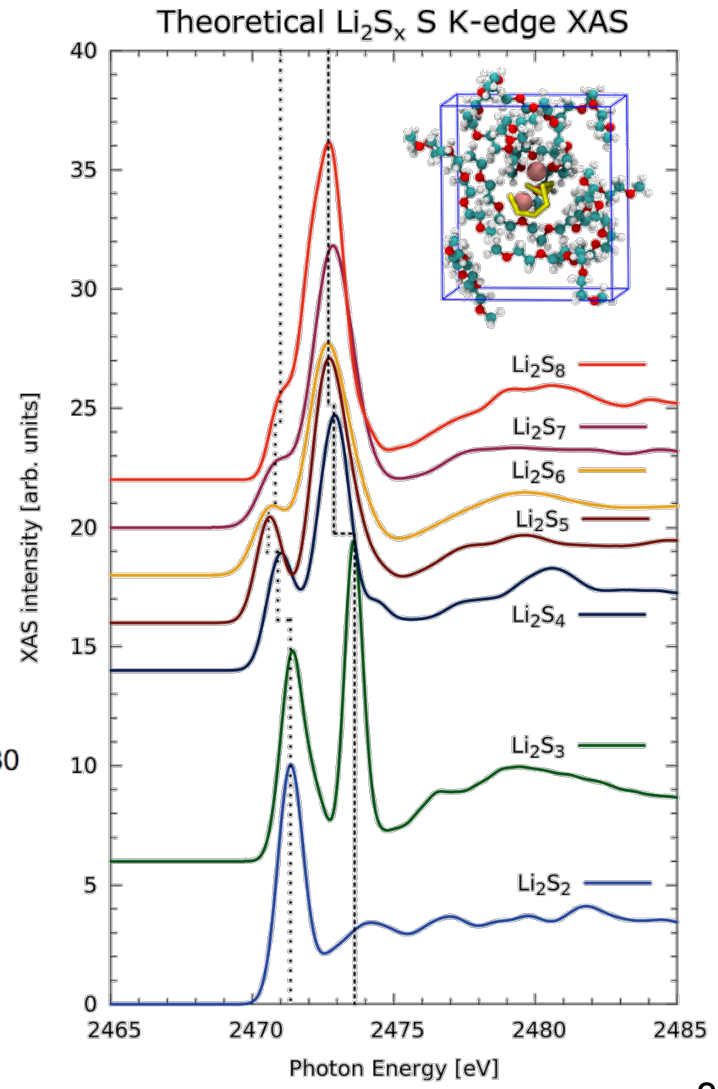
(In situ XAS Li-S cell)



1. Ultrathin Kapton film
2. O-ring
3. Spring
4. Stainless steel shim
5. Lithium metal
6. SEO/$LiClO_4$ electrolyte
7. Sulfur cathode
8. Aluminum mesh

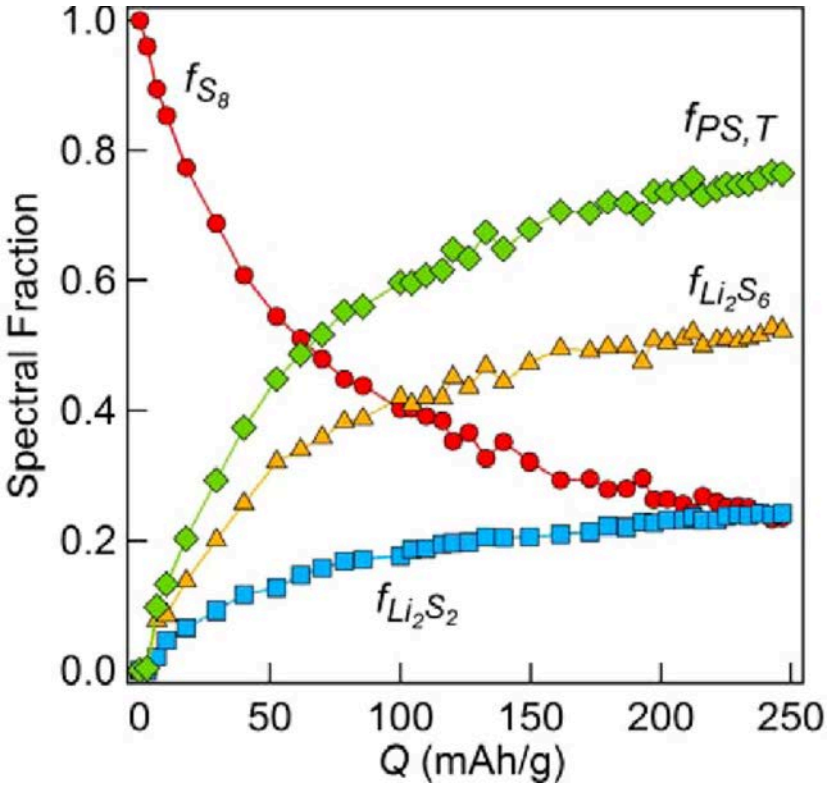
Technical Accomplishment: Performed in situ XAS experiments to directly probe cathode during discharge

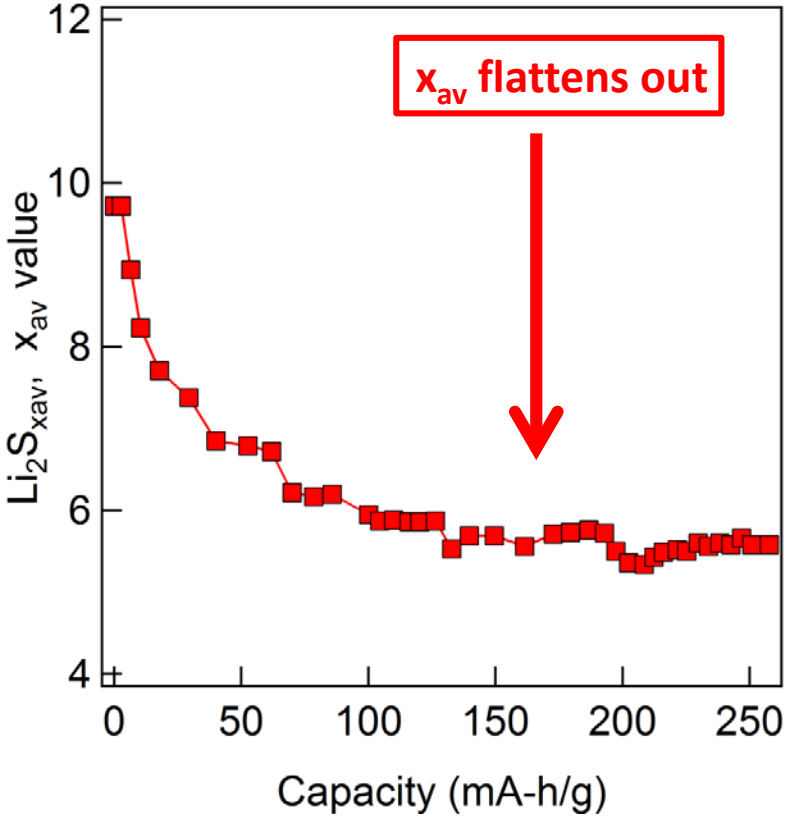




- Coupling experimental and theoretical spectra
- Sulfur K-edge XAS obtained at SSRL beamline 4-3
- Preliminary work performed at ALS beamline 9.3.1

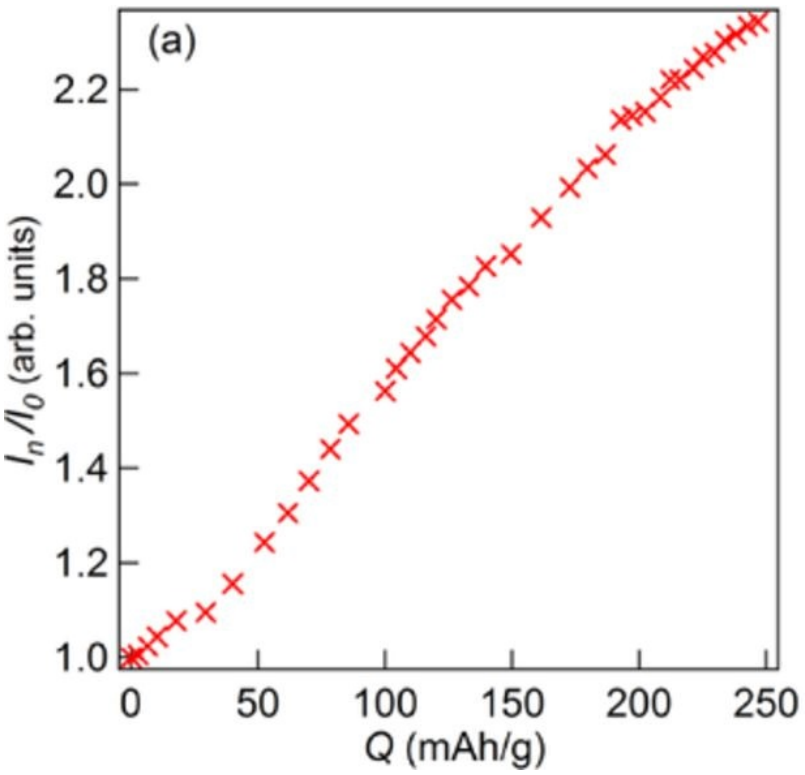
Technical Accomplishment: Consumption of elemental Sulfur at the back of the cathode

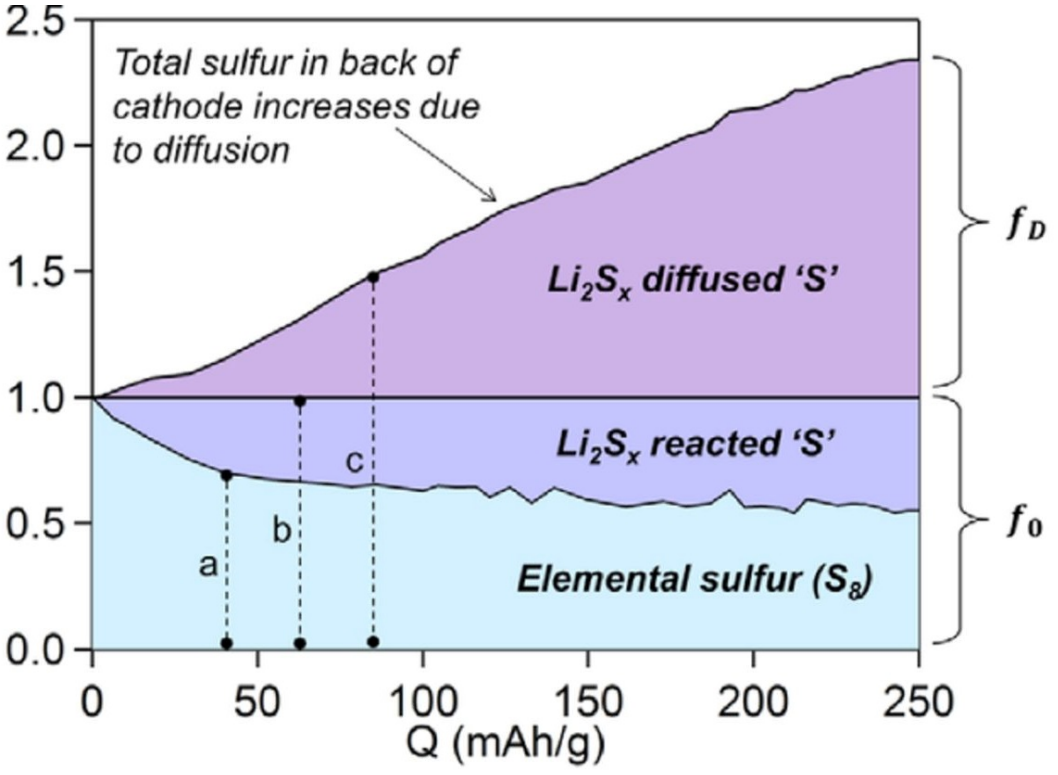




- Least squares fitting of experimental XAS spectra with theoretical spectra suggest elemental S is being consumed at the back of the cathode.
- The average polysulfide length initially decreases, but flattens out around Xav = 6 suggest that the reduction of S at the back of the cathode is far from complete

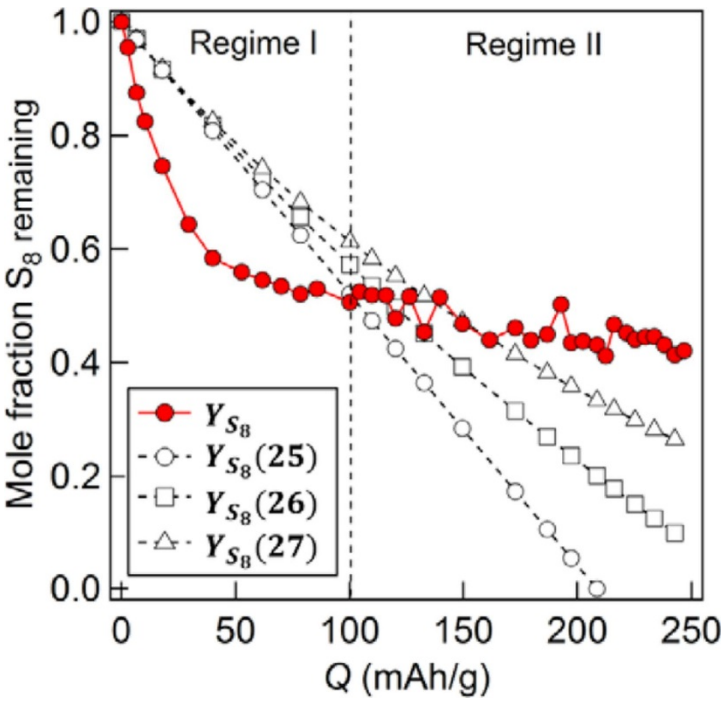
Technical Accomplishment: Polysulfide Diffusion into the Back of the Cathode

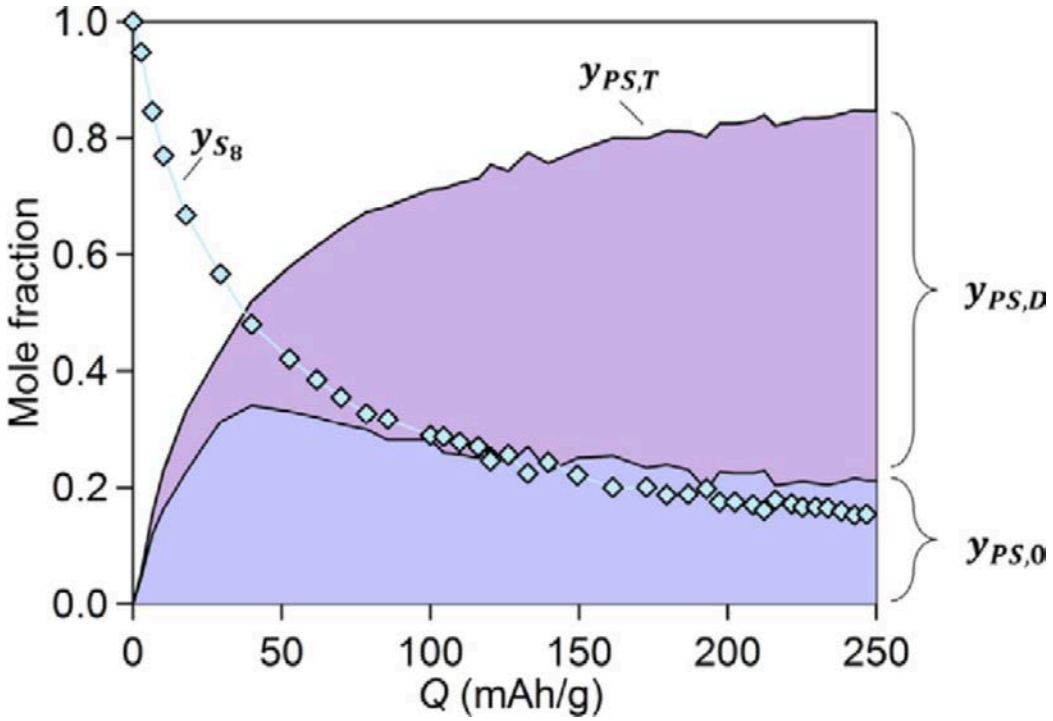




- The overall increase in fluorescence intensity indicates polysulfides formed at the front of the cathode are diffusing into the back of the cathode
- Polysulfides detected at the back of the cathode comes from 2 sources: (1) polysulfide diffused into the back of the cathode, and (2) polysulfides created at the back of the cathode

Technical Accomplishment: S consumption at the Back of the Cathode through both electrochemical and Chemical Reactions





- Elemental S at the back of the cathode is consumed both electrochemically and chemically
- The consumption of S at the back of the cathode is dominated by electrochemical reactions for 0 < Q < 50 mAh/g, and is dominated by chemical reactions for Q > 50 mAh/g.

Technical Accomplishment: Lithium Polysulfide Structures and Coordinations in DMF

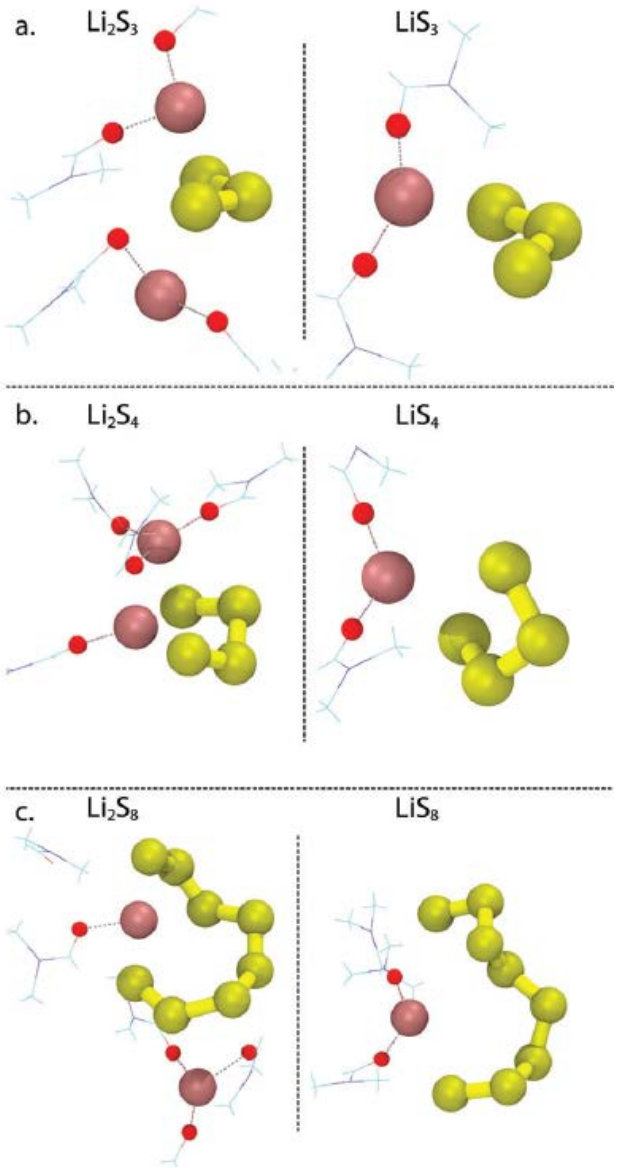


Table 1. Average Coordination number of Polysulfides in DMF

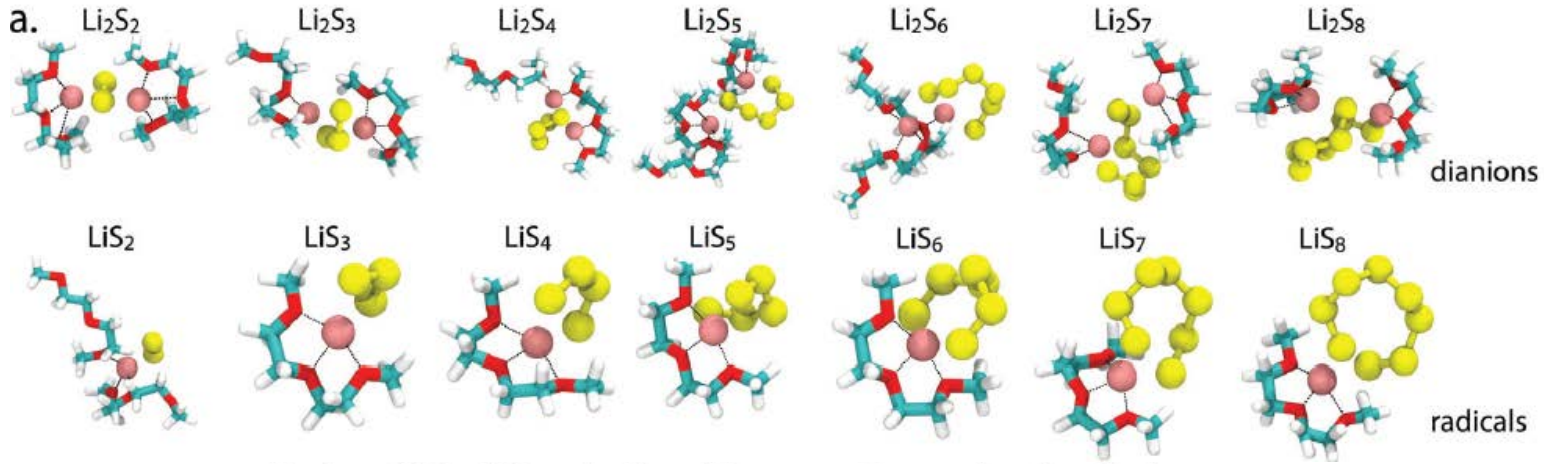
	Li^u – O	Li^b – O	Li^u - S	Li^b - S		Li - O	Li - S
Li_2S_2	1.99	1.95	2.96	2.56	LiS_2	2.53	2.68
Li_2S_3	1.99	1.98	1.42	1.68	LiS_3	2.37	1.44
Li_2S_4	2.26	1.85	0.88	1.36	LiS_4	2.54	1.96
Li_2S_5	2.86	1.18	0.68	2.20	LiS_5	2.36	1.96
Li_2S_6	2.98	1.14	0.54	2.42	LiS_6	2.42	1.92
Li_2S_7	3.00	1.18	0.50	2.48	LiS_7	2.48	1.96
Li_2S_8	3.00	0.99	0.50	2.58	LiS_8	2.55	2.04

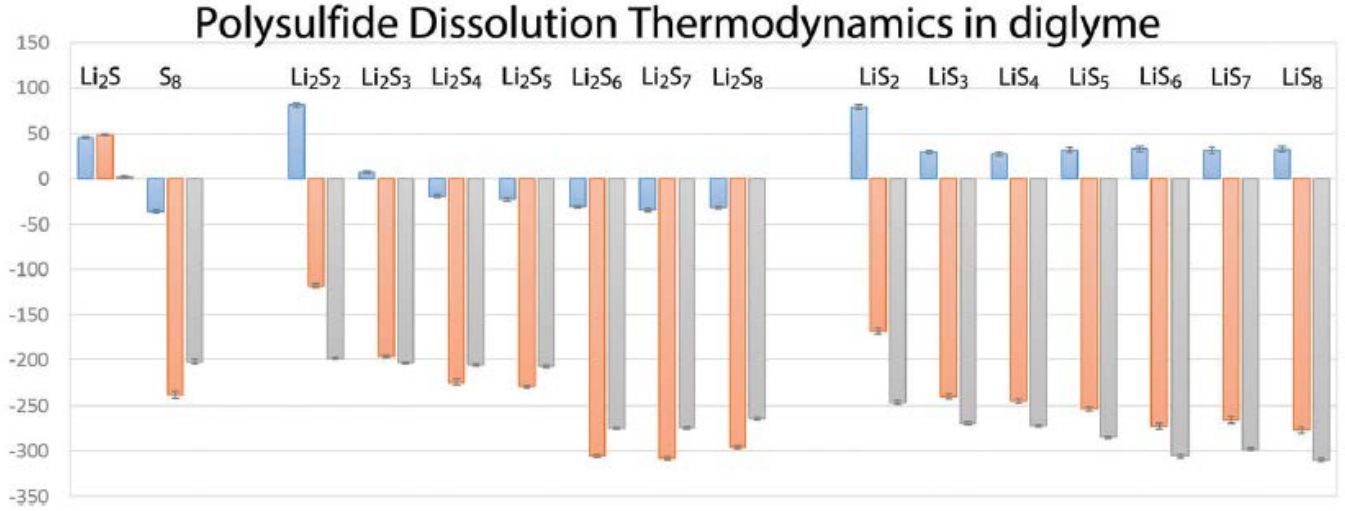
- Short-chain polysulfide dianions (Li_2S_2, Li_2S_3) exhibit quasi-tetrahedral coordination of lithium by 2 sulfur and 2 solvent oxygen atoms.
- Long-chain polysulfide dianions (Li_2S_x, $5 \leq x \leq 8$) exhibit reduced Li-S binding and reduced overall electrostatic repulsion between S and solvent.
- Radical anion coordination arrangements are relatively invariant with chain length

Technical Accomplishment: Lithium Polysulfide Dissolution Thermodynamics in DMF

- There is a significant loss of entropy associated with polysulfide dissolution, which compensates for increased lithium-solvent electrostatic interactions.
- The dissolution free energy (and thus solubility) of the dianions increases with increasing chain length.
- Most radicals are less soluble than the dianions due to the larger entropic loss.

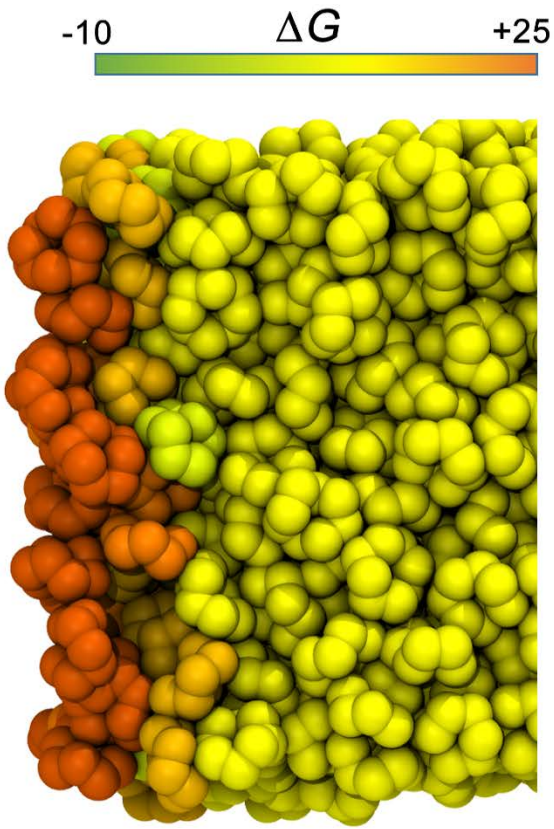
Technical Accomplishment: Lithium Polysulfide Structures and Thermodynamics in Diglyme

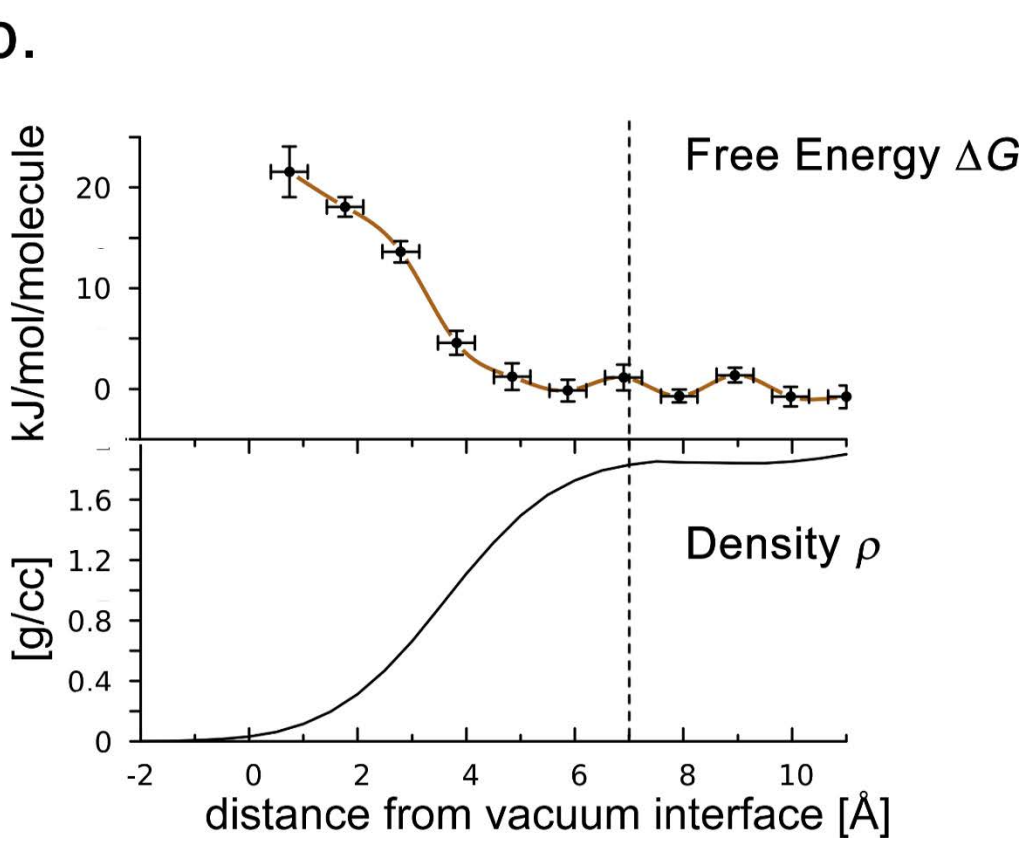




- Coordination arrangement varies less with chain length in diglyme
- The rigid solvent structure of diglyme molecules result in more pronounced losses in dissolution entropy, which greatly reduce the stability of dissolved lithium polysulfides, particularly that of the radical species in glyme based electrolytes.

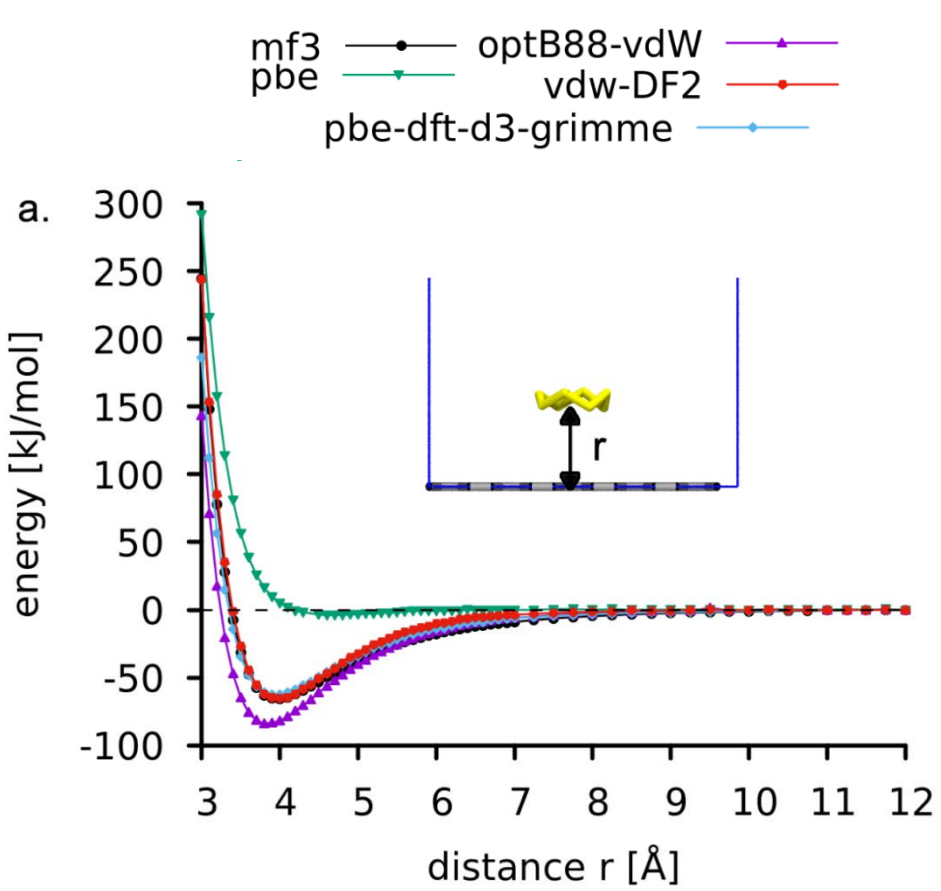
Technical Accomplishment: CMD Calculation of Sulfur/vapor interfacial thermodynamics

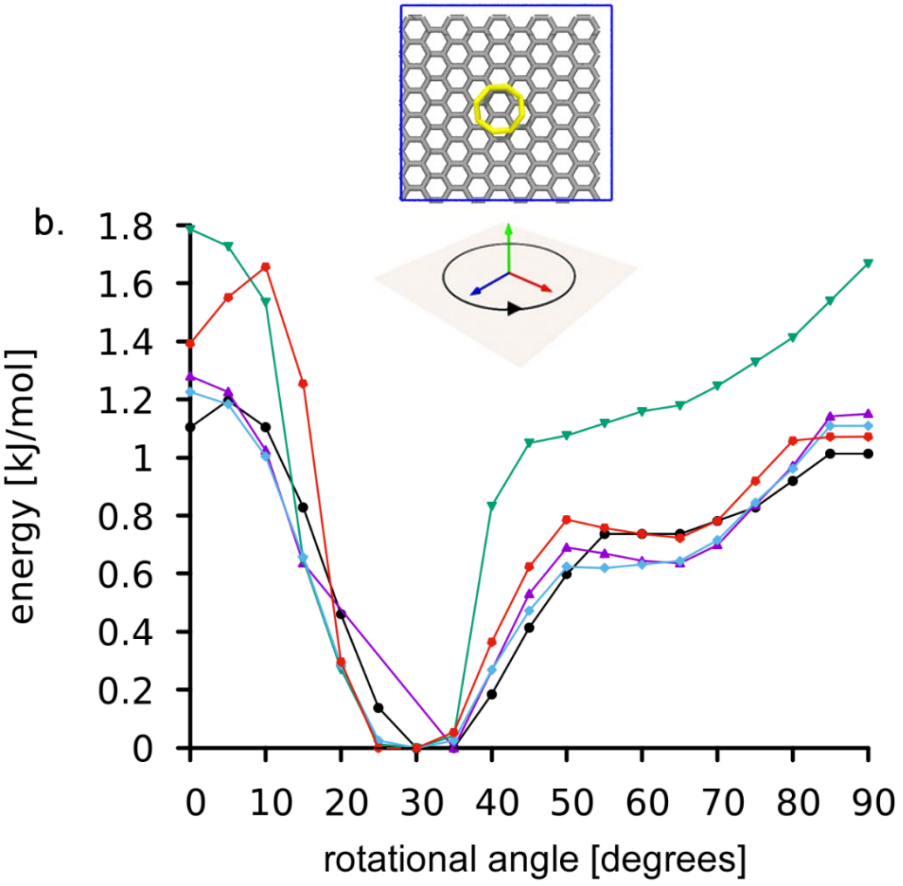




- Liquid Sulfur molecules at the vacuum interface are less stable than in the bulk at T_m.

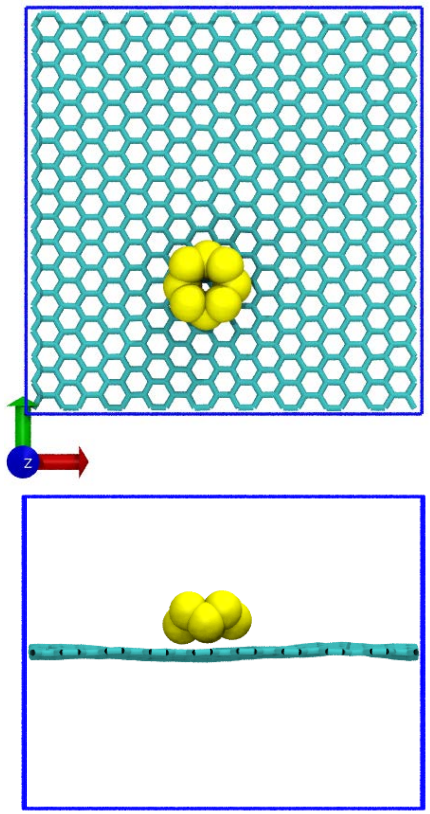
Technical Accomplishment: Nanoscale hydrophobic scaling: liquid Sulfur bind to Graphene

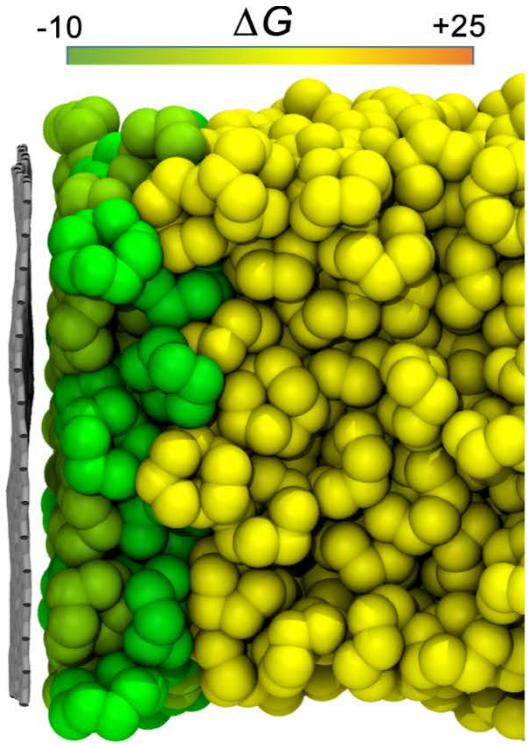


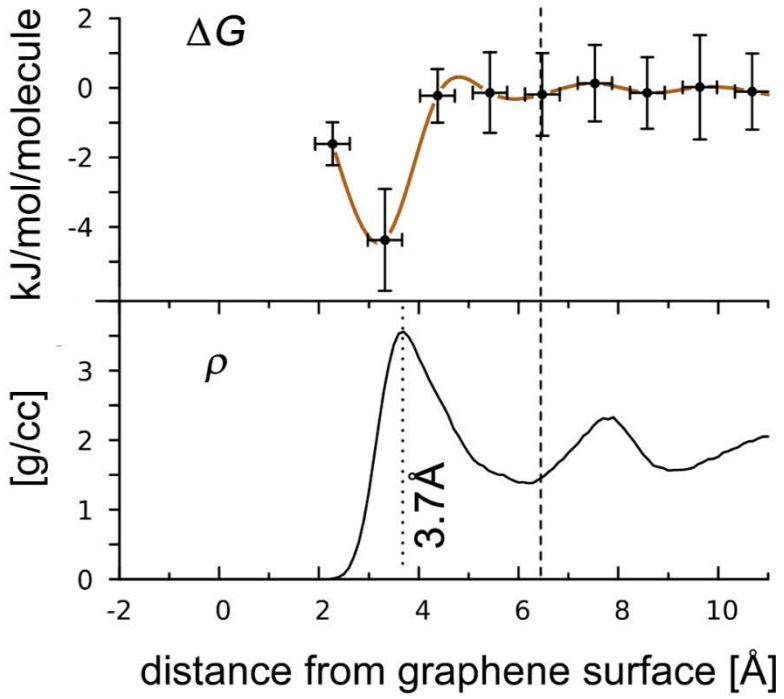


- Sulfur – Carbon interaction: binding energy of a single S_8 molecule over graphene

Technical Accomplishment: CMD Calculation of Sulfur/graphene interfacial thermodynamics

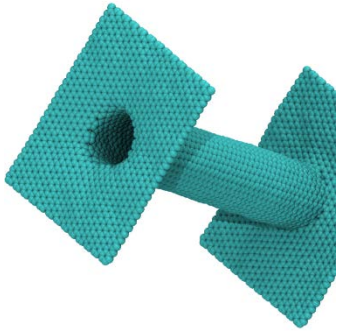


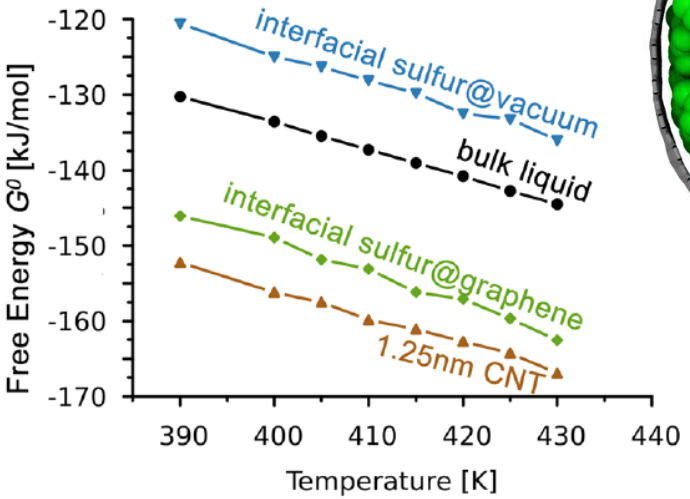


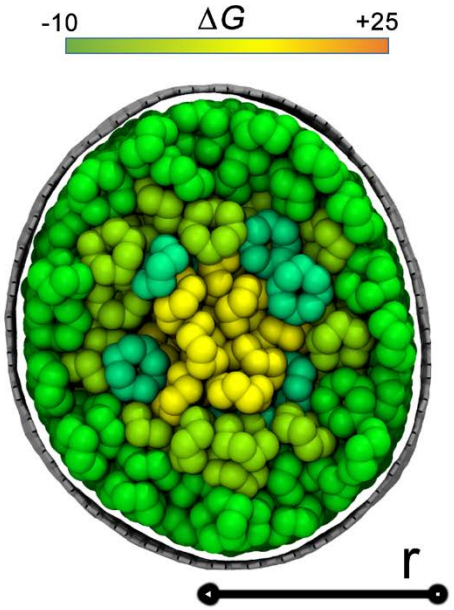


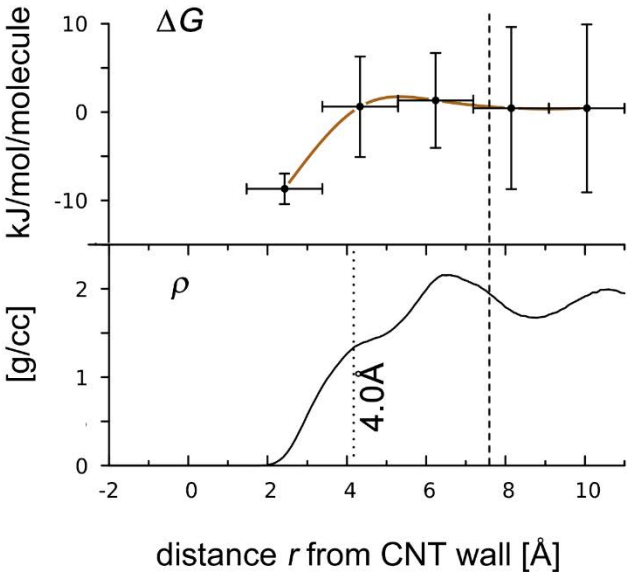
- Sulfur molecules at the graphene interface are more stable than in the bulk, leads to a natural wetting (low contact angle) behavior at T_m.

Technical Accomplishment: CMD Calculation of Sulfur/CNT interfacial thermodynamics



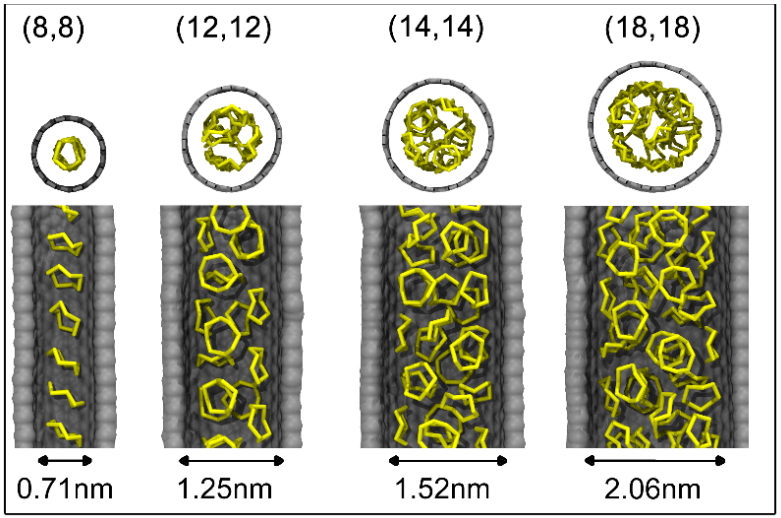


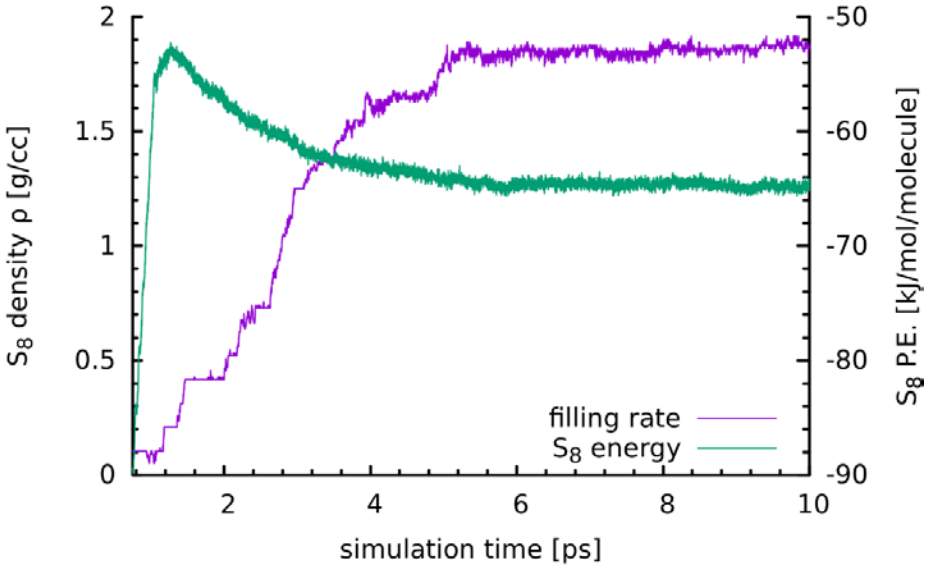


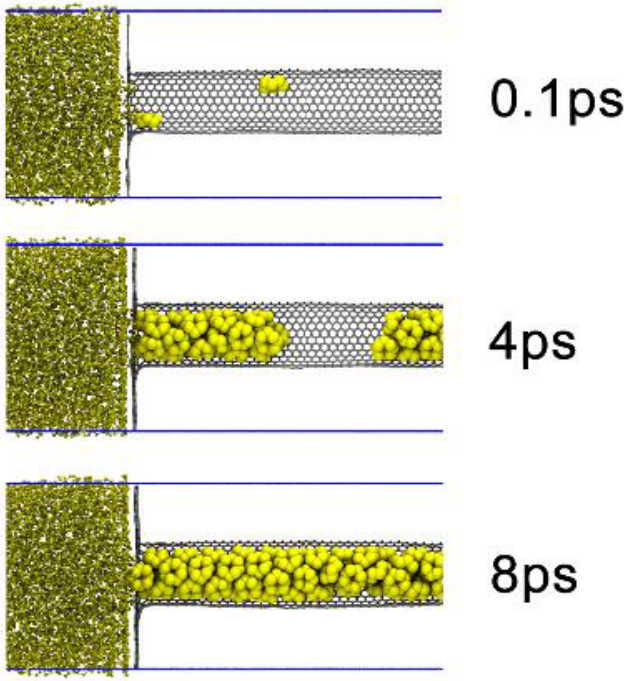


- Sulfur molecules in microporous carbon capillaries have even lower free energy than the ones just next to the graphene sheet

Technical Accomplishment: Spontaneous filling of CNT by Sulfur molecules

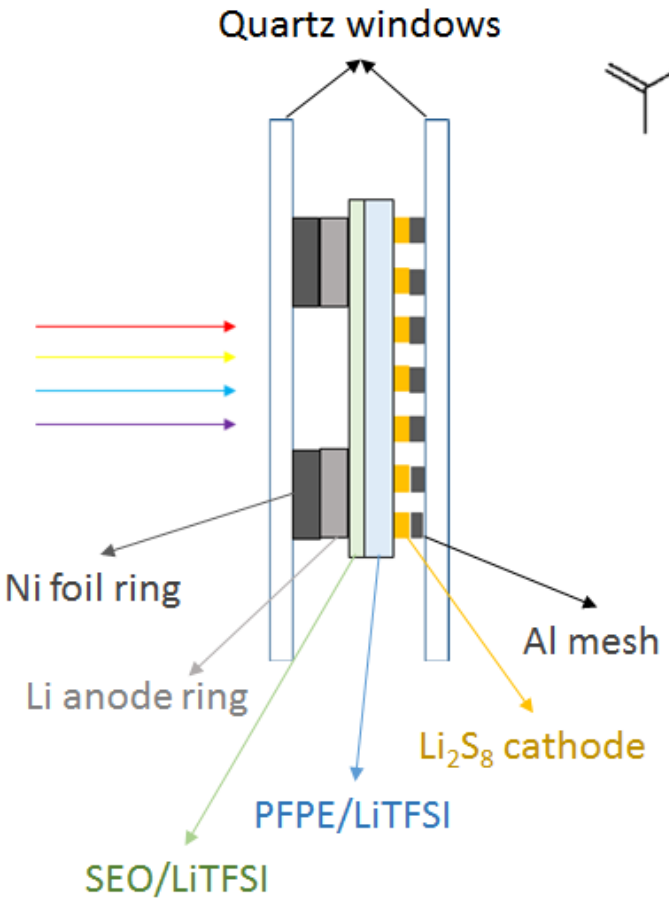


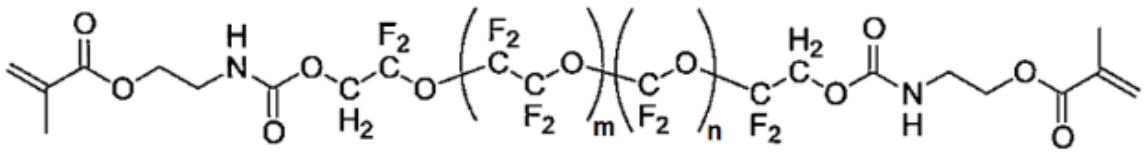


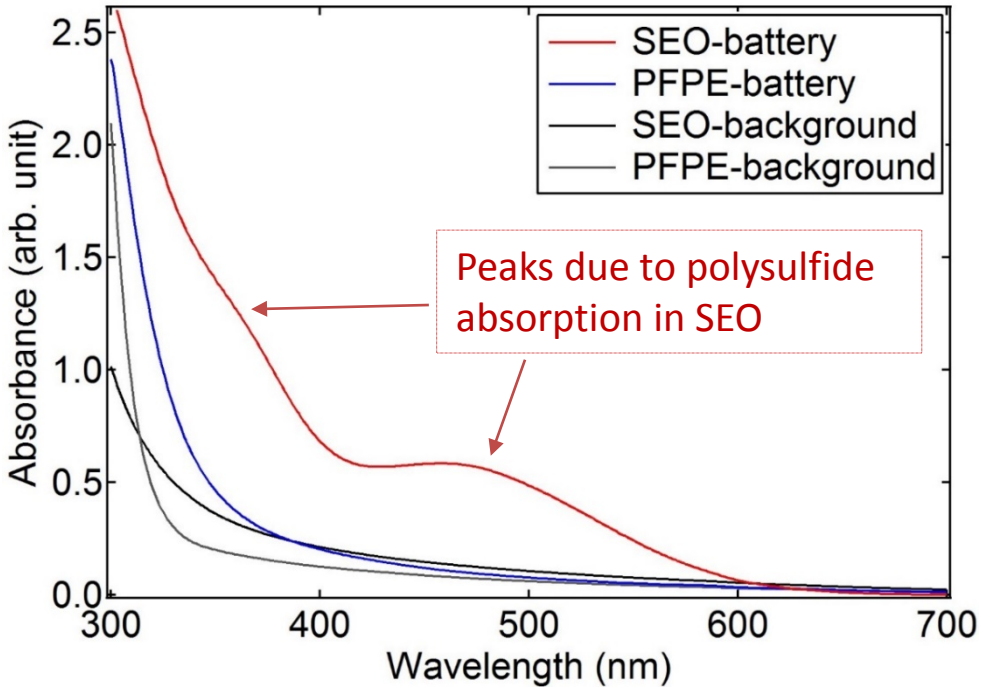


- Sulfur molecules are highly diffusive and spontaneously fill the CNT

Technical Accomplishment: New solid electrolyte Material Limits polysulfide diffusion







- Lack of polysulfide absorption peak using uv-vis in Li-S battery cycled with a PFPE electrolyte (compared to that using the SEO electrolyte only) indicates limited polysulfide diffusion into the electrolyte

Collaborators

- David Prendergast (Molecular Foundry, LBNL): Key co-PI on project in charge of theory and simulations. Advisor of post-doc BATT Program post-doc, Tod Pascal, Within VT program
- Kevin Wujcik and Dunyang Wang: graduate students advised by PI. Within VT program
- Wayne Stolte (National Security Technologies/SSRL): XAS measurements
- Erik Nelson (SSRL): XAS measurements
- Ethan Crumlin (ALS): XAS measurements
- Miquel Salmeron (Materials Sciences Division, LBNL): X-ray spectroscopy experiments. Outside VT program.
- Jinghua Guo (ALS, LBNL): X-ray spectroscopy instrumentation. Outside VT program.
- Feng Wang (BNL): Cathode characterization. Within VT program.
- Jeffrey Reimer (UC Berkeley): Electron paramagnetic resonance spectroscopy

Remaining Challenges and Barriers

- Determine species formed during cycling at different C-rates and in different cell configurations.
- Simulations of polysulfides under electrochemical potential.
- Use fundamental knowledge to build a better lithium-sulfur battery.

Future Work

- Continue *in situ* cell studies to determine reaction products as a function of C-rate and cathode thickness.
- Design simulations to study electrochemical reactions in sulfur cathode.
- Use fundamental knowledge to build a lithium-sulfur cell with long cycle life and high energy density.

Any future work is subject to change based on funding levels.

Summary

- Used simulations and *in situ* XAS measurements to determine the reactions in the back of a thick sulfur cathode during discharge of a Li-S battery.
- Elucidated the coordination arrangements and thermodynamics of lithium polysulfide species in different solvents using classical and first-principles MD methods
- Determined the interfacial interactions between sulfur and graphitic surfaces at a molecular scale that elucidated the critical morphology and thermodynamic properties necessary for future cathode design.
- Developed a new solid electrolyte system that limits lithium polysulfide diffusion which could potentially improve Li-S cell performance